

HYDROTREATING OF COMPONENTS FOR REFINERY BLENDING OF TRANSPORTATION FUELS

TECHNICAL FIELD

5 The present invention relates to fuels for transportation which are derived from natural petroleum, particularly processes for the production of components for refinery blending of transportation fuels which are liquid at ambient conditions. More specifically, it relates to integrated processes which include selective hydrogenation of high-boiling hydrogenation feedstock
10 whereby the incorporation of hydrogen into hydrocarbon compounds, sulfur-containing organic compounds, and/or nitrogen-containing organic compounds assists by hydrogenation removal of sulfur and/or nitrogen from components for refinery blending of transportation fuels. The integrated hydrotreating processes of this
15 invention advantageously provide their own source of high-boiling hydrogenation feedstock derived from other refinery units, for example, by fractionation of hydrotreated petroleum distillates.

Beneficially, the instant hydrotreating process is very selective, i.e. preferentially compounds in which a sulfur atom is
20 sterically hindered are hydrogenated rather than aromatic hydrocarbons. Products can be used directly as transportation fuels and/or blending components to provide, for example, more suitable components for blending into diesel fuels which are more friendly to the environment.

25 BACKGROUND OF THE INVENTION

It is well known that internal combustion engines have revolutionized transportation following their invention during the last decades of the 19th century. While others, including Benz and
30 Gottlieb Wilhelm Daimler, invented and developed engines using electric ignition of fuel such as gasoline, Rudolf C. K. Diesel invented and built the engine named for him which employs compression for auto-ignition of the fuel in order to utilize low-cost organic fuels. Development of improved diesel engines for use in transportation

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has proceeded hand-in-hand with improvements in diesel fuel compositions. Modern high performance diesel engines demand ever more advanced specification of fuel compositions, but cost remains an important consideration.

5 At the present time most fuels for transportation are derived from natural petroleum. Indeed, petroleum as yet is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. While compositions of natural petroleum or crude oils are significantly varied, all crudes contain sulfur compounds and
10 most contain nitrogen compounds which may also contain oxygen, but oxygen content of most crudes is low. Generally, sulfur concentration in crude is less than about 8 percent, with most crudes having sulfur concentrations in the range from about 0.5 to about 1.5 percent. Nitrogen concentration is usually less than 0.2
15 percent, but it may be as high as 1.6 percent.

Crude oil seldom is used in the form produced at the well, but is converted in oil refineries into a wide range of fuels and petrochemical feedstocks. Typically fuels for transportation are produced by processing and blending of distilled fractions from the
20 crude to meet the particular end use specifications. Because most of the crudes available today in large quantity are high in sulfur, the distilled fractions must be desulfurized to yield products which meet performance specifications and/or environmental standards. Sulfur containing organic compounds in fuels continue to be a major
25 source of environmental pollution. During combustion they are converted to sulfur oxides which, in turn, give rise to sulfur oxyacids and, also, contribute to particulate emissions.

Even in newer, high performance diesel engines combustion of conventional fuel produces smoke in the exhaust. Oxygenated
30 compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most such compounds have high vapor pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality, as indicated by
35 their cetane numbers. Furthermore, other methods of improving

diesel fuels by chemical hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel injectors and other moving parts which come in contact with the fuel under high pressures.

Distilled fractions used for fuel or a blending component of fuel for use in compression ignition internal combustion engines (Diesel engines) are middle distillates that usually contain from about 1 to 3 percent by weight sulfur. In the past a typical specifications for Diesel fuel was a maximum of 0.5 percent by weight. By 1993 legislation in Europe and United States limited sulfur in Diesel fuel to 0.3 weight percent. By 1996 in Europe and United States, and 1997 in Japan, maximum sulfur in Diesel fuel was reduced to no more than 0.05 weight percent. This world-wide trend must be expected to continue to even lower levels for sulfur.

In one aspect, pending introduction of new emission regulations in California and Federal markets has prompted significant interest in catalytic exhaust treatment. Challenges of applying catalytic emission control for the diesel engine, particularly the heavy-duty diesel engine, are significantly different from the spark ignition internal combustion engine (gasoline engine) due to two factors. First, the conventional three way catalyst (TWC) catalyst is ineffective in removing NOx emissions from diesel engines, and second, the need for particulate control is significantly higher than with the gasoline engine.

Several exhaust treatment technologies are emerging for control of Diesel engine emissions, and in all sectors the level of sulfur in the fuel affects efficiency of the technology. Sulfur is a catalyst poison that reduces catalytic activity. Furthermore, in the context of catalytic control of Diesel emissions, high fuel sulfur also creates a secondary problem of particulate emission, due to catalytic oxidation of sulfur and reaction with water to form a sulfate mist. This mist is collected as a portion of particulate emissions.

Compression ignition engine emissions differ from those of spark ignition engines due to the different method employed to initiate combustion. Compression ignition requires combustion of fuel droplets in a very lean air/fuel mixture. The combustion process leaves tiny particles of carbon behind and leads to significantly higher particulate emissions than are present in gasoline engines. Due to the lean operation the CO and gaseous hydrocarbon emissions are significantly lower than the gasoline engine. However, significant quantities of unburned hydrocarbon are adsorbed on the carbon particulate. These hydrocarbons are referred to as SOF (soluble organic fraction). Thus, the root cause of health concerns over diesel emissions can be traced to the inhalation of these very small carbon particles containing toxic hydrocarbons deep into the lungs.

While an increase in combustion temperature can reduce particulate, this leads to an increase in NO_x emission by the well-known Zeldovitch mechanism. Thus, it becomes necessary to trade off particulate and NO_x emissions to meet emissions legislation.

Available evidence strongly suggests that ultra-low sulfur fuel is a significant technology enabler for catalytic treatment of diesel exhaust to control emissions. Fuel sulfur levels of below 15 ppm, likely, are required to achieve particulate levels below 0.01 g/bhp-hr. Such levels would be very compatible with catalyst combinations for exhaust treatment now emerging, which have shown capability to achieve NO_x emissions around 0.5 g/bhp-hr. Furthermore, NO_x trap systems are extremely sensitive to fuel sulfur and available evidence suggests that they need would need sulfur levels below 10 ppm to remain active.

In the face of ever-tightening sulfur specifications in transportation fuels, sulfur removal from petroleum feedstocks and products will become increasingly important in years to come. While legislation on sulfur in diesel fuel in Europe, Japan and the U.S. has recently lowered the specification to 0.05 percent by weight (max.), indications are that future specifications may go far below the current 0.05 percent by weight level.

Conventional hydrodesulfurization (HDS) catalysts can be used to remove a major portion of the sulfur from petroleum distillates for the blending of refinery transportation fuels, but they are not efficient for removing sulfur from compounds where the sulfur atom is sterically hindered as in multi-ring aromatic sulfur compounds. This is especially true where the sulfur heteroatom is doubly hindered (e.g., 4,6-dimethyldibenzothiophene). Using conventional hydrodesulfurization catalysts at high temperatures would cause yield loss, faster catalyst coking, and product quality deterioration (e.g., color). Using high pressure requires a large capital outlay.

In order to meet stricter specifications in the future, such hindered sulfur compounds will also have to be removed from distillate feedstocks and products. There is a pressing need for economical removal of sulfur from distillates and other hydrocarbon products.

The art is replete with processes said to remove sulfur from distillate feedstocks and products. One known method involves the oxidation of petroleum fractions containing at least a major amount of material boiling above a very high-boiling hydrocarbon materials (petroleum fractions containing at least a major amount of material boiling above about 550° F.) followed by treating the effluent containing the oxidized compounds at elevated temperatures to form hydrogen sulfide (500° F. to 1350° F.) and/or hydroprocessing to reduce the sulfur content of the hydrocarbon material. See, for example, U.S. Patent Number 3,847,798 in the name of Jin Sun Yoo and U.S. Patent Number 5,288,390 in the name of Vincent A. Durante. Such methods have proven to be of only limited utility since only a rather low degree of desulfurization is achieved. In addition, substantial loss of valuable products may result due to cracking and/or coke formation during the practice of these methods. Therefore, it would be advantageous to develop a process which gives an increased degree of desulfurization while decreasing cracking or coke formation.

Several different oxygenation methods for improving fuels have been described in the past. For example, U.S. Patent Number 2,521,698 describes a partial oxidation of hydrocarbon fuels as improving cetane number. This patent suggests that the fuel should have a relatively low aromatic ring content and a high paraffinic content. U.S. Patent Number 2,912,313 states that an increase in cetane number is obtained by adding both a peroxide and a dihalo compound to middle distillate fuels. U.S. Patent Number 2,472,152 describes a method for improving the cetane number of middle distillate fractions by the oxidation of saturated cyclic hydrocarbon or naphthenic hydrocarbons in such fractions to form naphthenic peroxides. This patent suggests that the oxidation may be accelerated in the presence of an oil-soluble metal salt as an initiator, but is preferably carried out in the presence of an inorganic base. However, the naphthenic peroxides formed are deleterious gum initiators. Consequently, gum inhibitors such as phenols, cresols and cresylic acids must be added to the oxidized material to reduce or prevent gum formation. These latter compounds are toxic and carcinogenic.

U.S. Patent Number 4,494,961 in the name of Chaya Venkat and Dennis E. Walsh relates to improving the cetane number of raw, untreated, highly aromatic, middle distillate fractions having a low hydrogen content by contacting the fraction at a temperature of from 50° C. to 350° C. and under mild oxidizing conditions in the presence of a catalyst which is either (i) an alkaline earth metal permanganate, (ii) an oxide of a metal of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB or VIIIB of the periodic table, or a mixture of (i) and (ii). European Patent Application 0 252 606 A2 also relates to improving the cetane rating of a middle distillate fuel fraction which may be hydro-refined by contacting the fraction with oxygen or oxidant, in the presence of catalytic metals such as tin, antimony, lead, bismuth and transition metals of Groups IB, IIB, VB, VIB, VIIB and VIIIB of the periodic table, preferably as an oil-soluble metal salt. The application states that the catalyst selectively oxidizes benzylic carbon atoms in the fuel to ketones.

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Recently, U.S. Patent Number 4,723,963 in the name of William F. Taylor suggests that cetane number is improved by including at least 3 weight percent oxygenated aromatic compounds in middle distillate hydrocarbon fuel boiling in the range of 160° C. to 400° C. This patent states that the oxygenated alkylaromatics and/or oxygenated hydroaromatics are preferably oxygenated at the benzylic carbon proton.

More recently, oxidative desulfurization of middle distillates by reaction with aqueous hydrogen peroxide catalyzed by phosphotungstic acid and tri-*n*-octylmethylammonium chloride as phase transfer reagent followed by silica adsorption of oxidized sulfur compounds has been described by Collins et al. (Journal of Molecular Catalysis (A): Chemical 117 (1997) 397-403). Collins et al. described the oxidative desulfurization of a winter grade diesel oil which had not undergone hydrotreating. While Collins et al. suggest that the sulfur species resistant to hydrodesulfurization should be susceptible to oxidative desulfurization, the concentrations of such resistant sulfur components in hydrodesulfurized diesel may already be relatively low compared with the diesel oils treated by Collins et al.

U.S. Patent Number 5,814,109 in the name of Bruce R. Cook, Paul J. Berlowitz and Robert J. Wittenbrink relates to producing Diesel fuel additive, especially via a Fischer-Tropsch hydrocarbon synthesis process, preferably a non-shifting process. In producing the additive, an essentially sulfur free product of these Fischer-Tropsch processes is separated into a high-boiling fraction and a low-boiling fraction, e.g., a fraction boiling below 700° F. The high-boiling of the Fischer-Tropsch reaction product is hydroisomerized at conditions said to be sufficient to convert the high-boiling fraction to a mixture of paraffins and isoparaffins boiling below 700° F. This mixture is blended with the low-boiling of the Fischer-Tropsch reaction product to recover the diesel additive said to be useful for improving the cetane number or lubricity, or both the cetane number and lubricity, of a mid-distillate, Diesel fuel.

U.S. Patent Number 6,087,544 in the name of Robert J. Wittenbrink, Darryl P. Klein, Michele S Touvelle, Michel Daage and Paul J. Berlowitz relates to processing a distillate feedstream to produce distillate fuels having a level of sulfur below the distillate feedstream. Such fuels are produced by fractionating a distillate feedstream into a light fraction, which contains only from about 50 to 100 ppm of sulfur, and a heavy fraction. The light fraction is hydrotreated to remove substantially all of the sulfur therein. The desulfurized light fraction, is then blended with one half of the heavy fraction to product a low sulfur distillate fuel, for example 85 percent by weight of desulfurized light fraction and 15 percent by weight of untreated heavy fraction reduced the level of sulfur from 663 ppm to 310 ppm. However, to obtain this low sulfur level only about 85 percent of the distillate feedstream is recovered as a low sulfur distillate fuel product.

There is, therefore, a present need for catalytic processes to prepare oxygenated aromatic compounds in middle distillate hydrocarbon fuel, particularly processes, which do not have the above disadvantages. An improved process should be carried out advantageously in the liquid phase using a suitable oxygenation-promoting catalyst system, preferably an oxygenation catalyst capable of enhancing the incorporation of oxygen into a mixture of organic compounds and/or assisting by oxidation removal of sulfur or nitrogen from a mixture of organic compounds suitable as blending components for refinery transportation fuels liquid at ambient conditions.

This invention is directed to overcoming the problems set forth above in order to provide components for refinery blending of transportation fuels friendly to the environment.

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SUMMARY OF THE INVENTION

Economical processes are disclosed for the production of components for refinery blending of transportation fuels by selective hydrogenation of high-boiling hydrogenation feedstock derived, for example, by fractionation of hydrotreated petroleum distillates. The high-boiling hydrogenation feedstock is contacted with a gaseous source of dihydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst which exhibits a capability to enhance the incorporation of hydrogen into one or more of the sulfur-containing and/or nitrogen-containing organic compounds thereby assisting the removal of sulfur and/or nitrogen from the high-boiling feedstock. Products containing less sulfur and/or less nitrogen than the high-boiling hydrogenation feedstock are recovered from the reaction mixture. Advantageously, all or a portion of the product is blended with a low-boiling fraction of the hydrotreated distillate.

This invention contemplates the treatment of various type hydrocarbon materials, especially hydrocarbon oils of petroleum origin which contain sulfur. In general, the sulfur contents of the oils are in excess of 1 percent. 2 -3 percent

In one aspect, this invention provides a process for the production of fuel or blending component of fuels which are liquid at ambient conditions, which process comprises: (a) providing a high-boiling hydrogenation feedstock comprising a mixture of hydrocarbons and sulfur-containing organic compounds, the feedstock consisting essentially of material boiling between about 200° C. and about 425° C. and having a sulfur content up to about 2,500 ppm; (b) contacting the high-boiling feedstock with a gaseous source of dihydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst which exhibits a capability to enhance the incorporation of hydrogen into one or more of the sulfur-containing and/or nitrogen-containing organic compounds and under conditions suitable for hydrogenation of one or more of the sulfur-containing organic compounds; and (c) recovering a product comprising a mixture of hydrocarbons and other organic

compounds and having a sulfur content less than about 35 ppm of sulfur. Advantageously, the recovered product contains less than about 15 ppm of sulfur.

- Generally, useful hydrogenation catalysts comprise at least one active metal, selected from the *d*-transition elements in the Periodic Table, each incorporated onto an inert support in an amount of from about 0.1 percent to about 30 percent by weight of the total catalyst. Suitable active metals include the *d*-transition elements in the Periodic Table elements having atomic number in from 21 to 30, 39 to 48, and 72 to 78.

- In another aspect, this invention provides a process for the production of refinery transportation fuel or blending components for refinery transportation fuel having a sulfur content less than about 15 ppm, which process comprises: (1) hydrotreating a petroleum distillate consisting essentially of material boiling between about 50° C. and about 425° C. and having a sulfur content up to about 25,000 ppm, by a process which includes reacting the petroleum distillate with a source of hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated petroleum distillate, thereby producing a hydrotreated petroleum distillate having a sulfur content less than about 500 ppm; (2) fractionating the hydrotreated petroleum distillate by distillation to provide at least one low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction having a sulfur content less than about 15 ppm, and a high-boiling feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction containing the balance of the sulfur; (3) contacting the high-boiling feedstock with a gaseous source of dihydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst which exhibits a capability to enhance the incorporation of hydrogen into one or more of the sulfur-containing and/or nitrogen-containing organic compounds and under conditions suitable for hydrogenation of one or more of the sulfur-containing and/or nitrogen-containing organic compounds; (4) recovering a liquid comprising a mixture of hydrocarbons and other organic compounds, and having a sulfur

and/or nitrogen content less than the high-boiling feedstock; and (6) treating at least a portion of the recovered liquid with a solid sorbent, an ion exchange resin, and/or a suitable immiscible liquid containing a solvent or a soluble basic chemical compound, to obtain
5 a product having a sulfur content less than about 15 ppm.

In a further aspect of this invention, the hydrotreating of the petroleum distillate employs at least one bed of hydrogenation catalyst comprising one or more metals selected from the group consisting of cobalt, nickel, molybdenum and tungsten.

10 Advantageously, the contacting the high-boiling feedstock with a gaseous source of dihydrogen employs at least one bed of hydrogenation catalyst comprising one or more metals selected from the group consisting of nickel, molybdenum and tungsten.

In another aspect of this invention, the treating of recovered
15 liquid employs at least one bed of solid sorbent comprising alumina.

In yet another aspect, this invention provides a process for the producing a refinery transportation fuel or blending components for refinery transportation fuel having a sulfur content less than about 15 ppm, which process comprises: (I) providing a
20 refinery distillate comprising a mixture of hydrocarbons, sulfur-containing and nitrogen-containing organic compounds, the mixture having a sulfur content up to about 25,000 ppm and consisting essentially of material boiling between about 200° C. and about 425° C.; (II) hydrotreating the refinery distillate with a source of
25 hydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst to assist by hydrogenation removal of sulfur and/or nitrogen from the hydrotreated distillate, to recover a hydrotreated distillate having a sulfur content less than about 500 ppm; (III) fractionating the hydrotreated distillate by distillation to
30 provide at least one low-boiling blending component consisting of a sulfur-lean, mono-aromatic-rich fraction having a sulfur content less than about 15 ppm, and a high-boiling feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction containing the balance of the sulfur; (IV) contacting the high-boiling feedstock with a gaseous
35 source of dihydrogen at hydrogenation conditions in the presence of a hydrogenation catalyst which exhibits a capability to enhance the

incorporation of hydrogen into one or more of the sulfur-containing organic compounds and under conditions suitable for hydrogenation of one or more of the sulfur-containing organic compounds; and (V) recovering a high-boiling liquid having a sulfur content less than about 15 ppm.

Useful catalyst for the hydrotreating comprise a component capable to enhance the incorporation of hydrogen into a mixture of organic compounds to thereby form at least hydrogen sulfide, and a catalyst support component. The catalyst support component typically comprises a refractory inorganic oxide such as silica, alumina, or silica-alumina. Refractory inorganic oxides, suitable for use in the present invention, preferably have a pore diameter ranging from about 50 to about 200 Angstroms, and more preferably from about 80 to about 150 Angstroms for best results. Advantageously, the catalyst support component comprises a refractory inorganic oxide such as alumina.

Hydrotreating of the refinery distillate preferably employs at least one bed of hydrogenation catalyst comprising cobalt and one or more metals selected from the group consisting of nickel, molybdenum and tungsten, each incorporated onto an inert support in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst.

Contacting of the high-boiling feedstock with a gaseous source of dihydrogen preferably employs at least one bed of hydrogenation catalyst comprising nickel and one or more metals selected from the group consisting of, molybdenum and tungsten, each incorporated onto an inert support in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst.

In another aspect of this invention, the treating of recovered liquid employs at least one bed of solid sorbent comprising alumina.

In a further aspect of this invention, the process comprises treating at least a portion of the high-boiling liquid with a solid sorbent, an ion exchange resin, and/or a suitable immiscible liquid containing a solvent or a soluble basic chemical compound, to obtain

a high-boiling product having a sulfur content less than about 10 ppm.

In yet another aspect of this invention further comprises blending at least portions of the low-boiling blending component and the high-boiling product to form fuel for use in compression ignition internal combustion engines, and wherein the fuel exhibits a suitable flash point of at least 38° C. as measure by ASTM D93, and contains less than 15 ppm sulfur. In a further aspect of this invention, the fuel exhibits a suitable flash point of at least 49° C.

Beneficially processes of the invention further comprise blending at least portions of the low-boiling blending component and the high-boiling liquid to form fuel for use in compression ignition internal combustion engines, and wherein the fuel exhibits a suitable flash point of at least 38° C. as measure by ASTM D93, and contains less than 15 ppm sulfur.

This invention is particularly useful towards sulfur-containing organic compounds in the oxidation feedstock which includes compounds in which the sulfur atom is sterically hindered, as for example in multi-ring aromatic sulfur compounds. Typically, the sulfur-containing organic compounds include at least sulfides, heteroaromatic sulfides, and/or compounds selected from the group consisting of substituted benzothiophenes and dibenzothiophenes.

Hydrogenation catalysts beneficially contain a combination of metals. Preferred are hydrogenation catalysts containing at least two metals selected from the group consisting of cobalt, nickel, molybdenum and tungsten. More preferably, co-metals are cobalt and molybdenum or nickel and molybdenum. Advantageously, the hydrogenation catalyst comprises at least two active metals, each incorporated onto a metal oxide support, such as alumina in an amount of from about 0.1 percent to about 20 percent by weight of the total catalyst.

Where the hydrogenation feedstock is a high-boiling distillate fraction derived from hydrotreating of a refinery stream, the refinery stream consists essentially of material boiling between

compounds which are liquid at ambient conditions. Suitable refinery streams generally have an API gravity ranging from about 10° API to about 100° API, preferably from about 10° API to about 75 or 100° API, and more preferably from about 15° API to about 50° API for best results. These streams include, but are not limited to, fluid catalytic process naphtha, fluid or delayed process naphtha, light virgin naphtha, hydrocracker naphtha, hydrotreating process naphthas, alkylate, isomerate, catalytic reformat, and aromatic derivatives of these streams such as benzene, toluene, xylene, and combinations thereof. Catalytic reformat and catalytic cracking process naphthas can often be split into narrower boiling range streams such as light and heavy catalytic naphthas and light and heavy catalytic reformat, which can be specifically customized for use as a feedstock in accordance with the present invention. The preferred streams are light virgin naphtha, catalytic cracking naphthas including light and heavy catalytic cracking unit naphtha, catalytic reformat including light and heavy catalytic reformat and derivatives of such refinery hydrocarbon streams.

Suitable refinery distillate steams generally boil in a temperature range from about 50° C. to about 425° C., preferably 150° C. to about 400° C., and more preferably between about 175° C. and about 375° C. at atmospheric pressure for best results. These streams include, but are not limited to, virgin light middle distillate, virgin heavy middle distillate, fluid catalytic cracking process light catalytic cycle oil, coker still distillate, hydrocracker distillate, and the collective and individually hydrotreated embodiments of these streams. The preferred streams are the collective and individually hydrotreated embodiments of fluid catalytic cracking process light catalytic cycle oil, coker still distillate, and hydrocracker distillate.

It is also anticipated that one or more of the above distillate steams can be combined for use as a feedstock. In many cases performance of the refinery transportation fuel or blending components for refinery transportation fuel obtained from the various alternative feedstocks may be comparable. In these cases, logistics such as the volume availability of a stream, location of the

nearest connection and short term economics may be determinative as to what stream is utilized.

Typically, sulfur compounds in petroleum fractions are relatively non-polar, heteroaromatic sulfides such as substituted benzothiophenes and dibenzothiophenes. At first blush it might appear that heteroaromatic sulfur compounds could be selectively extracted based on some characteristic attributed only to these heteroaromatics. Even though the sulfur atom in these compounds has two, non-bonding pairs of electrons which would classify them as a Lewis base, this characteristic is still not sufficient for them to be extracted by a Lewis acid. In other words, selective extraction of heteroaromatic sulfur compounds to achieve lower levels of sulfur requires greater difference in polarity between the sulfides and the hydrocarbons.

Integrated processes of the invention optionally include one or more selective separation steps using solid sorbents. Non-limiting examples of such sorbents, commonly known to the skilled artisan, include activated carbons, activated bauxite, activated clay, activated coke, alumina, and silica gel. The liquid stream containing hydrogenated material is contacted with solid sorbent for a time sufficient to reduce the sulfur content of the hydrocarbon phase.

Integrated processes of the invention can include one or more selective separation steps using an immiscible liquid containing a soluble basic chemical compound. The sulfur containing hydrocarbon material is contacted with the solution of chemical base for a time sufficient to reduce the acid content of the hydrocarbon phase, generally from about 1 second to about 24 hours, preferably from 1 minute to 60 minutes. The reaction temperature is generally from about 10° C. to about 230° C., preferably from about 40° C. to about 150° C.

Generally, the suitable basic compounds include ammonia or any hydroxide, carbonate or bicarbonate of an element selected from Group I, II, and/or III of the periodic table, although calcined dolomitic materials and alkali aluminas can be used. In addition, mixtures of different bases can be utilized. Preferably the

basic compound is a hydroxide, carbonate or bicarbonate of an element selected from Group I and/or II element. More preferably, the basic compound is selected from the group consisting of sodium, potassium, barium, calcium and magnesium hydroxide, carbonate or bicarbonate. For best results processes of the present invention employ an aqueous solvent containing an alkali metal hydroxide, preferably selected from the group consisting of sodium, potassium, barium, calcium and magnesium hydroxide.

In carrying out a sulfur separation step according to this invention, pressures of near atmospheric and higher are suitable. While pressures up to 100 atmosphere can be used, pressures are generally in a range from about 15 psi to about 500 psi, preferably from about 25 psi to about 400 psi.

Useful distillate fractions for hydrogenation in the present invention consists essentially of any one, several, or all refinery streams boiling in a range from about 50° C. to about 425° C., preferably 150° C. to about 400° C., and more preferably between about 175° C. and about 375° C. at atmospheric pressure. The lighter hydrocarbon components in the distillate product are generally more profitably recovered to gasoline and the presence of these lower boiling materials in distillate fuels is often constrained by distillate fuel flash point specifications.

The distillate fractions for hydrogenation in the present invention can comprise high and low sulfur virgin distillates derived from high- and low-sulfur crudes, coker distillates, catalytic cracker light and heavy catalytic cycle oils, and distillate boiling range products from hydrocracker and resid hydrotreater facilities. Generally, coker distillate and the light and heavy catalytic cycle oils are the most highly aromatic feedstock components, ranging as high as 80 percent by weight. The majority of coker distillate and cycle oil aromatics are present as monoaromatics and diaromatics with a smaller portion present as triaromatics. Virgin stocks such as high and low sulfur virgin distillates are lower in aromatics content ranging as high as 20 percent by weight aromatics. Generally, the aromatics content of a

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combined hydrogenation facility feedstock will range from about 5 percent by weight to about 80 percent by weight, more typically from about 10 percent by weight to about 70 percent by weight, and most typically from about 20 percent by weight to about 60 percent by weight.

Sulfur concentration in distillate fractions for hydrogenation in the present invention is generally a function of the high and low sulfur crude mix, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher sulfur distillate feedstock components are generally virgin distillates derived from high sulfur crude, coker distillates, and catalytic cycle oils from fluid catalytic cracking units processing relatively higher sulfur feedstocks. These distillate feedstock components can range as high as 2.5 percent by weight elemental sulfur but generally range from about 0.1 percent by weight to about 0.9 percent by weight elemental sulfur.

Nitrogen content of distillate fractions for hydrogenation in the present invention is also generally a function of the nitrogen content of the crude oil, the hydrogenation capacity of a refinery per barrel of crude capacity, and the alternative dispositions of distillate hydrogenation feedstock components. The higher nitrogen distillate feedstocks are generally coker distillate and the catalytic cycle oils. These distillate feedstock components can have total nitrogen concentrations ranging as high as 2000 ppm, but generally range from about 5 ppm to about 900 ppm.

The catalytic hydrogenation process may be carried out under relatively mild conditions in a fixed, moving fluidized or ebullient bed of catalyst. Preferably a fixed bed of catalyst is used under conditions such that relatively long periods elapse before regeneration becomes necessary, for example an average reaction zone temperature of from about 200° C. to about 450° C., preferably from about 250° C. to about 400° C., and most preferably from about 275° C. to about 350° C. for best results, and at a pressure within the range of from about 6 to about 160 atmospheres.

A particularly preferred pressure range within which the hydrogenation provides extremely good sulfur removal while minimizing the amount of pressure and hydrogen required for the hydrodesulfurization step are pressures within the range of 20 to
5 60 atmospheres, more preferably from about 25 to 40 atmospheres.

According to the present invention, suitable distillate fractions are preferably hydrodesulfurized before being selectively oxidized, and more preferably using a facility capable of providing effluents of at least one low-boiling fraction and one high-boiling fraction.

10 Generally, the hydrogenation process useful in the present invention begins with a distillate fraction preheating step. The distillate fraction is preheated in feed/effluent heat exchangers prior to entering a furnace for final preheating to a targeted reaction zone inlet temperature. The distillate fraction can be
15 contacted with a hydrogen stream prior to, during, and/or after preheating.

The hydrogen stream can be pure hydrogen or can be in admixture with diluents such as hydrocarbon, carbon monoxide, carbon dioxide, nitrogen, water, sulfur compounds, and the like.
20 The hydrogen stream purity should be at least about 50 percent by volume hydrogen, preferably at least about 65 percent by volume hydrogen, and more preferably at least about 75 percent by volume hydrogen for best results. Hydrogen can be supplied from a hydrogen plant, a catalytic reforming facility or other hydrogen
25 producing process.

The reaction zone can consist of one or more fixed bed reactors containing the same or different catalysts. A fixed bed reactor can also comprise a plurality of catalyst beds. The plurality of catalyst beds in a single fixed bed reactor can also comprise the
30 same or different catalysts.

Since the hydrogenation reaction is generally exothermic, interstage cooling, consisting of heat transfer devices between fixed bed reactors or between catalyst beds in the same reactor shell, can be employed. At least a portion of the heat generated from the

hydrogenation process can often be profitably recovered for use in the hydrogenation process. Where this heat recovery option is not available, cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream injected directly into the reactors. Two-stage processes can provide reduced temperature exotherm per reactor shell and provide better hydrogenation reactor temperature control.

The reaction zone effluent is generally cooled and the effluent stream is directed to a separator device to remove the hydrogen. Some of the recovered hydrogen can be recycled back to the process while some of the hydrogen can be purged to external systems such as plant or refinery fuel. The hydrogen purge rate is often controlled to maintain a minimum hydrogen purity and remove hydrogen sulfide. Recycled hydrogen is generally compressed, supplemented with "make-up" hydrogen, and injected into the process for further hydrogenation.

Liquid effluent of the separator device can be processed in a stripper device where light hydrocarbons can be removed and directed to more appropriate hydrocarbon pools. Preferably the separator and/or stripper device includes means capable of providing effluents of at least one low-boiling liquid fraction and one high-boiling liquid fraction. Liquid effluent and/or one or more liquid fraction thereof is subsequently treated to incorporate oxygen into the liquid organic compounds therein and/or assist by oxidation removal of sulfur or nitrogen from the liquid products. Liquid products are then generally conveyed to blending facilities for production of finished distillate products.

Operating conditions to be used in the hydrogenation process include an average reaction zone temperature of from about 200° C. to about 450° C., preferably from about 250° C. to about 400° C., and most preferably from about 275° C. to about 350° C. for best results.

The hydrogenation process typically operates at reaction zone pressures ranging from about 400 psig to about 2000 psig, more preferably from about 500 psig to about 1500 psig, and most preferably from about 600 psig to about 1200 psig for best results.

Hydrogen circulation rates generally range from about 500 SCF/Bbl to about 20,000 SCF/Bbl, preferably from about 2,000 SCF/Bbl to about 15,000 SCF/Bbl, and most preferably from about 3,000 to about 13,000 SCF/Bbl for best results. Reaction pressures and
5 hydrogen circulation rates below these ranges can result in higher catalyst deactivation rates resulting in less effective desulfurization, denitrogenation, and dearomatization. Excessively high reaction pressures increase energy and equipment costs and provide diminishing marginal benefits.

10 The hydrogenation process typically operates at a liquid hourly space velocity of from about 0.2 hr⁻¹ to about 10.0 hr⁻¹, preferably from about 0.5 hr⁻¹ to about 3.0 hr⁻¹, and most preferably from about 1.0 hr⁻¹ to about 2.0 hr⁻¹ for best results. Excessively high space velocities will result in reduced overall
15 hydrogenation.

In a preferred embodiment of the invention, a petroleum distillate is passed to hydrotreater where is it hydrotreated in the presence of a hydrotreating catalyst to remove heteroatoms, particularly sulfur and to saturate aromatics.

20 Suitable catalysts for use in hydrotreating the petroleum distillate according to the present invention are any conventional hydrogenation catalyst used in the petroleum and petrochemical industries. A common type of such catalysts are those comprised of at least one active metal each incorporated onto an inert support.
25 Preferably, least one active metal is a Group VIII metal, more preferably a metal is selected from the group consisting of cobalt, nickel and iron, and most preferably a metal is selected from the group consisting of cobalt and nickel. Preferred catalysts are those comprised of at least one Group VIII metal and at least one Group
30 VI metal, preferably selected from the group consisting of molybdenum and tungsten. Preferably each incorporated onto a high surface area support material, such as alumina, silica alumina, and zeolites. The Group VIII metal is typically present in an amount ranging from about 2 percent to about 20 percent,
35 preferably from about 4 percent to about 12 percent based upon

the total weight of catalyst. The Group VI metal will typically be present in an amount ranging from about 5 percent to about 50 percent, preferably from about 10 percent to about 40 percent and more preferably from about 20 percent to about 30 percent based upon the total weight of catalyst. It is within the scope of the present invention that more than one type of hydrogenation catalyst be used in the same bed.

Suitable support materials used for catalysts according to the present invention include inorganic refractory materials, e.g., alumina, silica, silicon carbide, amorphous and crystalline silica-aluminas, silica magnesias, alumina-magnesias, boria, titania, zirconia and mixtures and co-gels thereof. Preferred support materials for the catalysts include alumina, amorphous silica-alumina, and the crystalline silica-aluminas, particularly those materials classified as clays or zeolites. The most preferred crystalline silica-aluminas are controlled acidity zeolites which are modified by their method of synthesis, for example by the incorporation of acidity moderators, and post-synthesis modifications such as dealumination.

Further reduction of such heteroaromatic sulfides from a distillate petroleum fraction by hydrotreating would require that the stream be subjected to very severe catalytic hydrogenation in order to convert these compounds into hydrocarbons and hydrogen sulfide (H_2S). Typically, the larger any hydrocarbon moiety is, the more difficult it is to hydrogenate the sulfide. Therefore, the residual organo-sulfur compounds remaining after a hydrotreatment are the most tightly substituted sulfides.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to better communicate the present invention, still another preferred aspect of the invention is depicted schematically in the drawing. Referring now to the schematic flow diagram, a substantially liquid stream of middle distillates from a refinery source 16 is charged through conduit 18 into catalytic reactor 20.

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A gaseous mixture containing dihydrogen (molecular hydrogen) is supplied to catalytic reactor 20 from storage or a refinery source 12 through manifold 14 and conduit 15. Catalytic reactor 20 contains one or more fixed bed of the same or different catalyst which have a hydrogenation-promoting action for desulfurization, denitrogenation, and dearomatization of middle distillates. The reactor may be operated in up-flow, down-flow, or counter-current flow of the liquid and gases through the bed.

One or more beds of catalyst and subsequent separation and distillation operate together as an integrated hydrotreating and fractionation system. This system separates unreacted dihydrogen, hydrogen sulfide and other non-condensable products of hydrogenation from the effluent stream and the resulting liquid mixture of condensable compounds is fractionated into a low-boiling fraction containing a minor amount of remaining sulfur and a high-boiling fraction containing a major amount of remaining sulfur.

Mixed effluents from catalytic reactor 20 are transferred into separation drum 24 through conduit 22. Unreacted dihydrogen, hydrogen sulfide and other non-condensed compounds flow from separation drum 24 through conduit 28 to hydrogen recovery (not shown). Advantageously, all or a portion of the unreacted hydrogen may be recycled to catalytic reactor 20, provided at least a portion of the hydrogen sulfide has been separated therefrom.

Hydrogenated liquids flow from separation drum 24 into distillation column 30 through conduit 26. Gases and condensable vapors from the top of column 30 are transferred through overhead cooler 40, by means of conduits 34 and 42, and into overhead drum 44. Separated gases and non-condensed compounds flow from overhead drum 44 to disposal or further recovery (not shown) through conduit 48. A portion of the condensed organic compounds suitable for reflux is returned from overhead drum 44 to column 30 through conduit 46.

The low-boiling fraction having the minor amount of sulfur-containing organic compounds is withdrawn from near the top of

column 30 and transferred to fuel blending facility 100 through conduit 32. This light fraction will typically represent that portion of the stream that contains less than about 50 ppm, preferably less than about 35 ppm, more preferably less than about 15 ppm sulfur, and most preferably less than about 5 ppm sulfur. It should be apparent that this low-boiling fraction from the catalytic hydrogenation is a valuable product in itself.

Beneficially, all or a portion of the low-boiling fraction in substantially liquid form is diverted through conduit 32a and into an optional oxygenation process unit 110 for catalytic oxidation in the liquid phase with a gaseous source of dioxygen, such as air or oxygen enriched air. For the purpose of the present invention, the term "oxygenation" is defined as any means by which one or more atoms of oxygen is added to a hydrocarbon molecule. Particularly suitable catalytic oxygenation processes are disclosed in commonly assigned U.S. Patent Application Serial Number (37,248A) and U.S. Patent Application Serial Number (37,248B).

A stream containing oxygenated organic compounds is subsequently separated to recover, for example, a fuel or a blending component of fuel and transferred to fuel blending facility 100 through conduit 32b. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

A portion of the high-boiling liquid at the bottom of column 30 is transferred to reboiler 36 through conduit 35, and a stream from reboiler 36 is returned to distillation column 30 through conduit 37.

From the bottom of column 30 another portion of the high-boiling liquid fraction having the major amount of the sulfur-containing organic compounds is supplied to exchanger 50 through conduit 38 and manifold 52. From exchanger 50 the high-boiling liquid fraction is supplied to as feedstock to hydrogenation reactor 60 through conduit 56 and manifold 58. Also a gaseous mixture containing dihydrogen (makeup hydrogen) is supplied to manifold 54 from manifold 14 through conduit 54.

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Typically a fixed bed of suitable catalyst is used in reactor 60 under conditions such that relatively long periods elapse before regeneration becomes necessary, for example an average reaction zone temperature of from about 200° C. to about 450° C., preferably from about 250° C. to about 400° C., and most preferably from about 275° C. to about 350° C. for best results, and at a pressure within the range of from about 6 to about 160 atmospheres.

A mixture of effluents from hydrogenation reactor 60 is transferred into separation drum 64 through conduit 62. Gaseous compounds, including unreacted dihydrogen, are recycled to hydrogenation reactor 60 from separation drum 64 through conduit 68 and manifold 58. A purge stream of unreacted dihydrogen, hydrogen sulfide and other non-condensed compounds is taken from separation drum 64 through conduit 65 to hydrogen recovery (not shown). Optionally, steam is supplied to column 70 from refinery source 67 through conduit 72.

Hydrogenated liquids flow from separation drum 64 into distillation column 70 through conduit 66. Gases and condensable vapors from the top of column 70 are transferred through overhead cooler 80, by means of conduits 74 and 82, and into overhead drum 84. Separated gases and non-condensed compounds flow from overhead drum 84 to disposal or further recovery (not shown) through conduit 88. A portion of the condensed organic compounds suitable for reflux is returned from overhead drum 84 to column 70 through conduit 86. Other portions of the condensate are beneficially recycled from overhead drum 84 to separation drum 64 and/or transferred to other refinery uses (not shown) through conduit 87. Aqueous condensate is transferred to water treatment (not shown) from separation drum 84 through conduit 85.

A portion of the liquid near the bottom of column 70 is withdrawn and transferred to reboiler 76 through conduit 75, and a stream of vapor from reboiler 76 is returned to distillation column 70 through conduit 77.

From the bottom of column 70 a crude hydrotreated high-boiling liquid fraction is supplied to vessel 90 through conduit 78. Vessel 90 contains a bed of solid sorbent which exhibits the ability to retain acidic and/or other polar compounds, to obtain product containing less sulfur and/or less nitrogen than the feedstock to the oxidation. Product is transferred from vessel 90 to fuel blending facility 100 through conduit 92. Preferably, in this embodiment a system of two or more reactors containing solid sorbent, configured for parallel flow, is used to allow continuous operation while one bed of sorbent is regenerated or replaced.

In view of the features and advantages of processes in accordance with this invention using selected organic peracids in a liquid phase reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds to preferentially oxidize compounds in which a sulfur atom is sterically hindered rather than aromatic hydrocarbons, as compared to known desulfurization systems previously used, the following examples are given. The following examples are illustrative and are not meant to be limiting. Unless otherwise indicated, percentages and ppm are on the bases of an appropriate weight.

EXAMPLE 1

In this example a refinery distillate containing sulfur at a level of about 500 ppm was hydrotreated under conditions suitable to produce hydrodesulfurized distillate containing sulfur at a level of about 130 ppm, which was identified as hydrotreated distillate 150. Hydrotreated distillate 150 was cut by distillation into four fractions which were collected at temperatures according to the following schedule.

Fraction	Temperatures, °C
1	Below 260
2	260 to 288
3	288 to 316
4	Above 316

Analysis of hydrotreated distillate 150 over this range of distillation cut points is shown in Table I. In accordance with this invention a fraction collected below a temperature in the range from about 260° C. to about 300° C. splits hydrotreated distillate 150 into a sulfur-lean, monoaromatic-rich fraction and a sulfur-rich, monoaromatic-lean fraction.

Table I
ANALYSIS OF DISTILLATION FRACTIONS OF HYDROTREATED
DISTILLATE 150

		Fraction Number			
Item		1	2	3	Total
Weight, %		45	21	19	100
Sulfur, ppm		11.7	25	174	133
Mono-Ar, %		40.7	26.3	15.6	28.8
Di-Ar, %		0.4	5.0	5.4	3.1
Tri-Ar, %		0	0	0	0.1

Mono-Ar is mono-aromatics. Di-Ar is di-aromatics. Tri-Ar is tri-aromatics.

EXAMPLE 2

In this example a refinery distillate containing sulfur at a level of about 500 ppm was hydrotreated under conditions suitable to produce a hydrodesulfurized distillate containing sulfur at a level of about 15 ppm, which was identified as hydrotreated distillate 15.

Analysis of hydrotreated distillate 15 over the range of distillation cut points is shown in Table II. In accordance with this invention a fraction collected below a temperature in the range from about 260° C. to about 300° C. splits hydrotreated distillate 15 into a sulfur-lean, monoaromatic-rich fraction and a sulfur-rich, monoaromatic-lean fraction.

Table II
ANALYSIS OF DISTILLATION FRACTIONS OF
HYDROTREATED DISTILLATE 15

		Fraction Number				
5	Item	1	2	3	4	Total
	Weight, %	53	16	20	11	100
	Sulfur, ppm	1	2	13	80	12.3
	Mono-Ar, %	35.8	20.9	14.8	12.0	5.6
	Di-Ar, %	1.3	8.0	7.4	5.6	4.0
10	Tri-Ar, %	0	0	0	1.4	0.2

Mono-Ar is mono-aromatics. Di-Ar is di-aromatics. Tri-Ar is tri-aromatics.

15 EXAMPLE 3

Hydrotreated refinery distillate S-25 was partitioned by distillation to provide feedstock for oxidation using hydrogen peroxide and acetic acid. The fraction collected below temperatures of about 300° C. was a sulfur-lean, monoaromatic-rich fraction identified as S-25-B300. Analyses of S-25-B300 determined a sulfur content of 3 ppm, a nitrogen content of 2 ppm, and 36.2 percent mono-aromatics, 1.8 percent di-aromatics, for a total aromatics of 37.9 percent. The fraction collected above temperatures of about 300° C. was a sulfur-rich, monoaromatic-poor fraction identified as S-25-A300. Analyses of S-25-A300 determined a sulfur content of 35 ppm, a nitrogen content of 31 ppm, and aromatic content was 15.7 percent mono-aromatics, 5.8 percent di-aromatics, and 1.4 percent tri-aromatics, for a total aromatics of 22.9 percent.

30 EXAMPLE 4

Hydrotreated refinery distillate S-25 was partitioned by distillation to provide feedstock for hydrogenation. The fraction of S-25 collected above temperatures of about 316° C. was a sulfur-

rich, monoaromatic-poor fraction identified as S-25-A316. Analyses of S-25-A316 determined a sulfur content of 80 ppm and a nitrogen content of 102 ppm.

EXAMPLE 5

- 5 A hydrotreated refinery distillate identified as S-150 was partitioned by distillation to provide feedstock for hydrogenation. Analyses of S-150 determined a sulfur content of 113 ppm and a nitrogen content of 36 ppm. The fraction of S-150 collected above temperatures of about 316° C. was a sulfur-rich, monoaromatic-
- 10 poor fraction identified as S-150-A316. Analyses of S-150-A316 determined a sulfur content of 580 ppm and a nitrogen content of 147 ppm.

EXAMPLE 6

- 15 Another hydrotreated refinery distillate identified as S-DF was partitioned by distillation to provide feedstock for hydrogenation. The fraction of S-DF collected below temperatures of about 288° C. was a sulfur-lean, monoaromatic-rich fraction identified as S-DF-B288. The fraction of S-DF collected above temperatures of about 288° C. was a sulfur-rich, monoaromatic-
- 20 poor fraction identified as S-DF-A288. Analyses of S-DF-A288 determined a sulfur content of 30 ppm.

EXAMPLE 7

- 25 A hydrotreated distillate from another commercial refinery source was identified as W-DDU-1227 and analyzed. Analyses of W-DDU-1227 determined a sulfur content of 417 ppm. Results of distillation according to ASTM D-86 for the hydrotreated distillate are presented in Table III. Hydrotreated distillate W-DDU-1227 was further analyzed by gas chromatograph to identify the boiling
- 30 point of the sulfur-containing compounds, and these results are presented in Table IV.

These data show that a hydrotreated distillate from commercial refinery source can be partitioned by distillation to provide low-boiling fraction which is substantially free of sulfur-

containing organic compounds, and a sulfur-rich, high-boiling fraction.

Table III

5 ASTMD-86 ANALYSIS OF HYDROTREATED
DISTILLATE W-DDU-1227

Temperature, °C.	214	244	266	318	333
Percent	10	30	50	90	95

10 Percent is based on total weight of the hydrotreated distillate.

Table IV

ANALYSIS FOR BOILING POINT OF SULFUR COMPOUNDS
IN HYDROTREATED DISTILLATE W-DDU-1227

15 BPt, °C.	340	342	351	357	368	379	398	419
Percent S	0.5	5	10	30	50	70	90	95

Percent S is based on total weight of sulfur in the distillate.

20 For the purposes of the present invention, "predominantly" is defined as more than about fifty percent. "Substantially" is defined as occurring with sufficient frequency or being present in such proportions as to measurably affect macroscopic properties of an associated compound or system. Where the frequency or

25 proportion for such impact is not clear, substantially is to be regarded as about twenty per cent or more. The term "a feedstock consisting essentially of" is defined as at least 95 percent of the feedstock by volume. The term "essentially free of" is defined as absolutely except that small variations which have no more than a

30 negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.